HTPB POLYMER IMPROVEMENT

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Lockheed Propulsion Company

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LOCKHEED PROPULSION COMPANY
REDLANDS, CALIFORNIA

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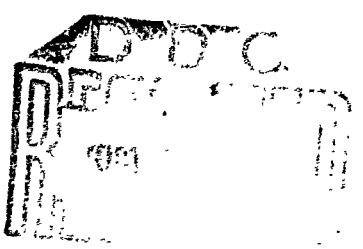

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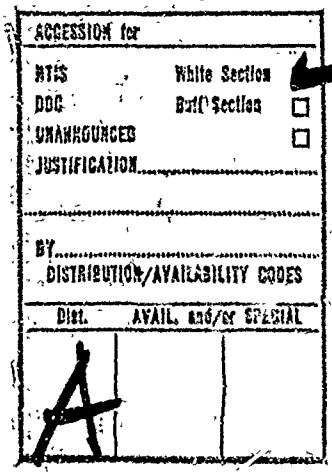

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13. ABSTRACT

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FOREWORD

This is the second Technical Summary Report issued under Contract F04611-72-C-0038, "HTPB Polymer Improvement", a program being conducted by Lockheed Propulsion Company, Redlands, California, and monitored by the Air Force Rocket Propulsion Laboratory (Robert L. Limoges, Second Lieutenant, MKPA, Program Monitor). The program is being conducted in cooperation with the manufacturer of the R-45 HTPB prepolymer: the Atlantic Richfield Corporation (ARCO), Philadelphia, Pennsylvania; and with the Government Research Laboratory, Esso Research and Engineering, Linden, New Jersey. Participating technical personnel are Dr. W. E. Baumgartner (Program Manager), Dr. G. E. Myers (Project Engineer), W. D. Allan and W. E. Heikkila at Lockheed Propulsion Company; Dr. P. W. Ryan and K. C. Ramey at ARCO; and A. E. Muenker at Esso.

Publication of this report does not constitute Air Force approval of the report's findings and conclusions. It is published only for the exchange and stimulation of ideas.

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Second Lieutenant
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ABSTRACT

From among the laboratory preparations of modified R-45M HTPB prepolymer that were previously examined, four were produced in a pilot plant for evaluation in 90-percent solids propellant. The pilot plant samples covered a molecular weight range from 2700 to 4100 and possessed weight average functionalities between 2.0 and 2.1. Propellant processability in each case was inferior to that of standard R-45M. On the basis of tensile properties and crack propagation tests, no distinctive differences in propellant mechanical behavior were apparent. Detailed comparison of thermal cycling behavior will be made in the final program phase.

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GLOSSARY

ARCO	Atlantic Richfield Corporation
B, C, E, F, G, K, L, M, N, N', O, P, Q	Laboratory preparations of prepolymer
EOM	End of mix
Esso	Government Research Laboratory, Esso Research and Engineering
$\bar{f}_n$	Number average functionality
$\bar{f}_w$	Weight action functionality
GPC	Gel permeation chromatography
HTPE	Hydroxy-terminated polybutadiene
IPDI	Isophorane diisocyanate
KP	Kilopoise
LPC	Lockheed Propulsion Company
$\overline{M}_n$	Number average molecular weight
$\overline{M}_w$	Weight average molecular weight
MT-4	Bonding agent
NCO/OH	Isocyanate to hydroxyl equivalents ratio
p	poise
RR	Round Robin R-45M. Lot 110225
R-45M	ARCO HTPB. Free radical polymerized
TSI	Toluene sulfonyl isocyanate
VPO	Vapor phase osmometer
η	Prepolymer viscosity in poise
σ_m/ϵ_m	Stress and strain at maximum load (stress)
σ_b/ϵ_b	Stress and strain at rupture

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SECTION I

INTRODUCTION

The commercially available ARCO R-45M HTPB prepolymer is being extensively studied for applications in highly loaded solid propellants and possesses some advantage over CTPB prepolymers in those systems. It does have some deficiencies, however, in potlife control and in balancing mechanical properties at low and high temperatures, which presumably are caused by the material's low molecular weight ($\overline{M}_n \sim 3000$), high functionality ($f_w \sim 2.3$), and high reactivity of its functional groups.

This program was established to determine whether the available variations in ARCO's free radical polymerization process could produce a modified R-45M possessing superior characteristics for use in solid propellants. In the program ARCO was to prepare 11 prepolymer samples under laboratory conditions/scale, each sample representing specific variations in their polymerization process. Those samples were to be characterized by both ARCO and Esso and evaluated in propellant on a small scale by LPC. Subsequently, three of those prepolymer lots were to be scaled up to the pilot plant level, characterized, and evaluated for propellant performance.

The first report under the program described the results of the characterization and evaluation of the laboratory samples (Ref 1). Those samples possessed a wide range of average molecular weight and average functionality. Their propellants also exhibited a wide range of processability, controlled primarily by molecular weight. However, propellant tensile properties generally showed relatively minor variations among the samples, i.e., molecular weight and functionality had little effect upon tensile behavior.

From the available data three prepolymers were selected for scaleup, covering the molecular weight range from about 2500 to 4000 and possessing functionalities very close to 2.0. This report describes the characterization and evaluation of the pilot plant samples.

(Ref 1). Baumgartner, W.E. and Myers, G.E., HTPB Polymer Improvement, AFRPL-TR-72-50, LPC Report No. 625-I-1, June 1972

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SECTION II

SUMMARY

From the polymerization process conditions previously employed in producing 14 laboratory samples of R-45M type prepolymers, ARCO has used four conditions on the pilot plant scale to produce four prepolymers at the 25- to 50-pound level. These were characterized analytically by ARCO and Esso, and evaluated by LPC in 90-percent solids propellant (Oronite-6 plasticizer, IPDI curative, with and without MT-4).

The analytical results are summarized as follows:

- Reproducibility between pilot plant and laboratory preparations is excellent.
- $\overline{M}_n$ varied from 2700 to 4100 with $\bar{f}_w$ values between 2.0 to 2.1.
- Solvent precipitation fractionation took place on the basis of molecular weight and/or equivalent weight, with some indication that $\bar{f}_w$ increases with $\overline{M}_n$.

Evaluation in propellant showed the following:

- Processability of the pilot plant samples was inferior to that of standard R-45M. However, this may be at least partially the consequence of higher impurity levels occasioned by incomplete pilot plant cleanup.
- No clear superiority over standard R-45M was observed from tensile properties or from crack propagation tests. (Some indication of improved thermal cycling capability was obtained from feasibility tests of a simultaneous strain/temperature cycling procedure, but these results must still be regarded with caution.)

However, this somewhat unexpected failure of material having higher molecular weight and functionalities close to two, to produce improved propellant mechanical behavior could be the consequence of relying largely upon uniaxial tensile tests for the mechanical properties evaluation. The last phase of the program will evaluate in greater detail the thermal cycling capability of propellants prepared from three of the pilot plant prepolymers.

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SECTION III

RESULTS

1. PREPOLYMER PREPARATION AND CHARACTERIZATION

Four prepolymers were prepared in the ARCO pilot plant at approximately the 50-pound level; three of them were prepared under conditions duplicating those used for the laboratory samples F, G, and R*, while the fourth (S-2) involved a further process modification. Initial preparations contained unacceptably high iron levels due to reactor startup problems. The repeat preparations tended toward higher iron levels than possessed by the laboratory samples but were regarded as satisfactory for the program. After preparation, all samples were stored under nitrogen in air-tight containers. Pilot plant samples have been designated F-2, G-2, R-2, and S-2 to distinguish them from the laboratory samples F, G, etc.

a. Analytical Results

The samples were characterized by number average molecular weight, analytical GPC, equivalent weight, number average and weight average functionality, viscosity, and impurities using methods described in the previous report (Ref 1). In addition, preparative scale fractionations were conducted by solvent precipitation at ARCO and the fractions also were characterized.

Table I summarizes the analysis results for the pilot plant samples, and Table II compares several parameters for pilot plant versus laboratory preparations. The following points are noted:

- $\overline{M}_n$ varies from about 2700 to 4100 and polydispersities are nearly equal.
- $\bar{f}_n$ values are all 2.0 within experimental error whereas values of $\bar{f}_w$ are between 2.0 and 2.1.
- S-2 appears to be equivalent to R-2.
- Reproducibility between laboratory and pilot plant is excellent.

ARCO separated each of the pilot plant samples into three fractions by addition of methanol to a 10-percent cyclohexane/acetone solution at 25°C. Table III summarizes the analytical values for the fractions and Table IV compares the corresponding parameters for each of the original prepolymers with those calculated from the fractionation data. The fractionation obviously took place on the basis of both $\overline{M}_n$ and equivalent weight. Table III indicates that $\bar{f}_w$ increases with molecular weight, but some doubt is cast upon that conclusion by the comparison of measured and observed $\bar{f}_w$

* A tabulation of analytical results obtained for the laboratory samples is included as Appendix A for reference purposes.

TABLE I

ANALYTICAL CHARACTERIZATION OF PILOT PLANT SAMPLES

Sample	Lab	$\bar{M}_n$ VPO	$\bar{M}_n$ GPC	M_w/M_n (GPC)	Eq Wt[a]	$\bar{f}_n$	$\bar{f}_w$[b]	η (p, 30°C)	H_2O (ppm)	Fe (ppm)	Peroxide (meq/1000 g)	Volatiles (%)
F-2	ARCO	4050	3910	1.65	2000	2.02	2.02	104	500	1	15	0.1
	Esso	4110			2110	1.95	2.03					
	Avg	4080			2060	1.99	2.03					
G-2	ARCO	2960	2840	1.57	1450 (1610)[c]	2.04	2.04	50	300	8	15	0.1
	Esso	3060			1520	2.01	2.11					
	Avg	3010			1490	2.03	2.08					
R-2	ARCO	2760	2630	1.52	1430	1.93	2.03	42	300	1	20	0.1
	Esso	2750			1400	1.96	2.09					
	Avg	2760			1420	1.94	2.06					
S-2	ARCO	2730	2600	1.5	1430	1.90	2.03	38	500	2	15	0.1
	Esso	2670			1390	1.92	2.06					
	Avg	2700			1410	1.91	2.05					

(a) TSI

(b) Procedure modified by addition of catalyst to permit completion in 8 hours rather than several hundred hours.

(c) Acetic anhydride

TABLE II

COMPARISON OF ANALYTICAL PARAMETERS:
LABORATORY VERSUS PILOT PLANT SAMPLES

Sample	Parameter[a] $\bar{M}_n$[b]	Eq Wt[c]	$\tilde{f}_n$	$\tilde{f}_w$[d]
F	4100/4080 (-1%)[e]	2270/2060 (-9%)	1.81/1.99 (+10%)	2.03/2.03 (0)
G	3100/3010 (-3%)	1770/1490 (-15%)	1.75/2.03 (+16%)	2.04/2.08 (+2%)
R	2530/2760 (+9%)	1220/1420 (+16%)	2.08/1.94 (-7%)	2.10/2.03 (-3%)

(a) Laboratory/pilot plant

(b) VPO

(c) TSI

(d) Laboratory samples without catalyst. Pilot plant samples with catalyst.

(e) Percent change from laboratory to pilot plant.

TABLE III

SOLVENT PRECIPITATION FRACTIONATION OF PILOT PLANT SAMPLES

Fraction	Weight Percent	$\overline{M}_n$ VPO	$\overline{M}_n$ GPC	Equivalent Weight (TSI)	f_n	f_w
F-2						
1	20	2160	2100	1090	1.99	2.02
2	60	5300(4650)	4280	2380(2930)	2.20(1.95)	2.16(2.16)
3	20	5800	4720	2440	2.38	2.24
G-2						
1	27	1890	1950	940	2.02	2.02
2	58	4180(3555)	3660	1890(1860)	2.22(1.91)	2.15(2.22)
3	15	4720	4300	1960	2.41	2.35
R-2						
1	20	1570	1530	670	2.36	2.05
2	60	3320(3230)	3000	1750(1640)	1.90(1.97)	2.02(2.17)
3	20	4350	3730	1920	2.26	2.20
S-2						
1	24	1620	1770	760	2.12	2.08
2	58	3430(3660)	3000	1750(1710)	1.96(2.14)	2.06(2.12)
3	18	3900	3540	1960	1.99	2.15

( ) = Esso values

in Table IV, which indicates that some modification of the fractions may have occurred during their preparation. Such modification, however, did not significantly affect molecular and equivalent weights.

b. Parameter Correlation

The first interim report presented crossplots for a number of the measured prepolymer parameters to determine what correlations might exist. Figures 1 and 2 illustrate two such plots when data points for the pilot plant samples are included. Figure 1 demonstrates that both laboratory and pilot plant samples follow the same $\eta/\overline{M}_n$ relationship, and Figure 2 confirms that the ARCO polymerization process can vary molecular weight and functionality independently.

2. EVALUATION IN PROPELLANT

The four pilot plant prepolymer samples and a control (standard R-45M, Lot 008281) were evaluated at the 1-gallon mix scale in propellant containing 90-percent solids, 3-percent Oronite-6 plasticizer, and cured with IPDI. The evaluation was made at a minimum of two NCO/OH ratios with MT-4 bonding agent, and at one NCO/OH ratio without MT-4. Cure was at 160^0F for 7 days.

a. Propellant Processability

The propellants were processed in a 1-gallon vertical Baker-Perkins mixer modified with a bottom discharge valve for casting directly from the mixer. A 170-minute mix cycle was employed, including 90 minutes after completing the addition of solids and 30 minutes final mix after curative addition. The end-of-mix (EOM) and potlife viscosities were determined by means of a Brookfield viscometer and a T-F bar. Table V summarizes the viscosity data.

As expected, much higher propellant viscosities were observed in the propellants containing MT-4 than in those that had no bonding agent. Where MT-4 was present, all of the pilot plant samples had EOM viscosities higher than those of the control (except sample S-2 at an NCO/OH ratio of 1.05). The relationship between prepolymer $\overline{M}_n$ and the relative EOM viscosity of the pilot plant samples is presented in Figure 3, along with the previous data for the laboratory samples. Within the data scatter, EOM viscosity is controlled generally by prepolymer $\overline{M}_n$, with deviations probably occasioned by reactivity differences.

Table VI lists the relative mix viscosities 3 hours after EOM for the formulations containing MT-4. These values were obtained by smoothing the data from Table VI and are judged to be accurate to ±0.05-0.1. Processability therefore is in the order of Control > F, R > G, S. It is possible, however, that the poorer processability of the pilot plant samples to some extent may be due to their relatively high iron content. As noted earlier this is a temporary deficiency that should be obviated in further production. In the present study, no casting difficulties were encountered with any of the test formulations.

TABLE IV

COMPARISON OF MEASURED AND CALCULATED PARAMETERS FOR SOLVENT PRECIPITATED FRACTIONATION

	$\overline{M}_n$		Equivalent Weight		$\bar{f}_w$	
Sample	Measured[(a)]	Calculated[(b)]	Measured	Calculated[(c)]	Measured	Calculated[(d)]
F-2	4080	4161(3904)[(e)]	2060	1932(2127)	2.03	2.15(2.15)
G-2	3010	3191(2960)	1490	1491(1480)	2.08	2.14(2.19)
R-2	2760	2824(2784)	1420	1341(1301)	2.06	2.06(2.15)
S-2	2700	2752(2835)	1410	1353(1339)	2.05	2.08(2.12)

(a) VPO

(b) $$M_n = \frac{1}{\sum \frac{w_i}{M_{n_i}}}$$

(c) $$\text{Eq Wt} = \frac{1}{\sum \frac{w_i}{E_i}}$$

(d) $$f_w = \Sigma\, w_i f_{w_i}$$

(e) ( ) indicates values calculated using Esso's values for mid-fraction

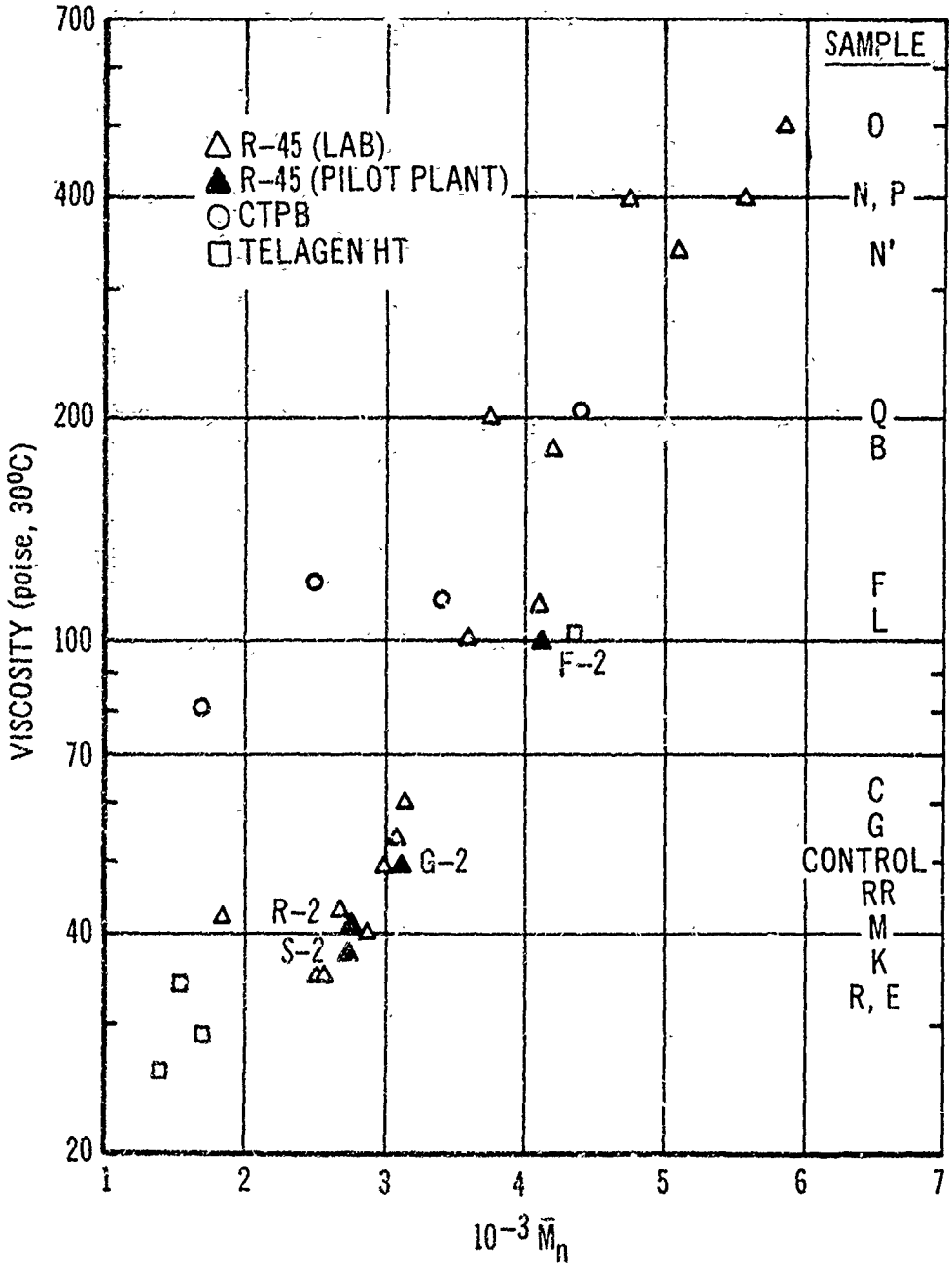

Figure 1 Prepolymer Viscosity versus $\bar{M}_n$

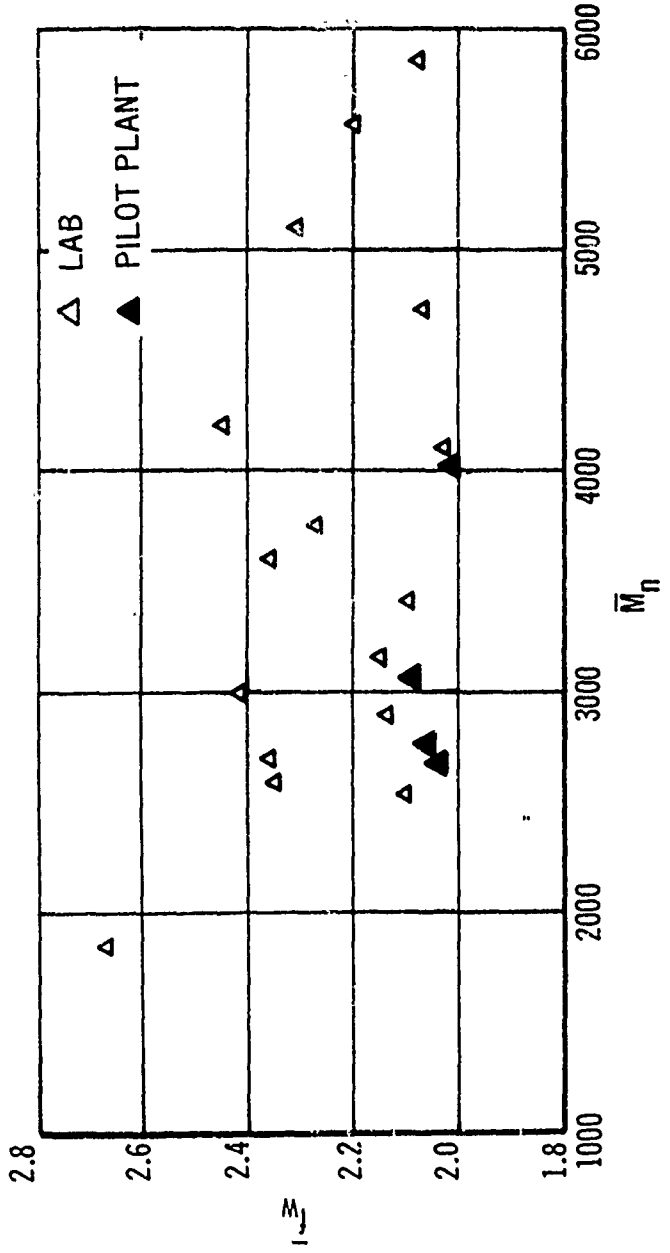

Figure 2 Prepolymer $\bar{f}_w$ versus $\bar{M}_n$

TABLE V

PROPELLANT PROCESSABILITY (90% SOLIDS);
VISCOSITY (KP AFTER HOURS)[a]

Sample	NCO/OH	EOM	Hours ½	1	1½	2	3	4	5
Control	0.80	28							
(Lot 008281)	0.80 - No MT-4	14							
	0.75	32	34			43	43	44	
F-2	0.95	42	55		58	56	56		
	0.95 - No MT-4	12	54		60	60	64		
	1.00	46							
G-2	0.85	48			69	74		65	
	0.85 - No MT-4	19							
	0.90	40							
R-2	0.90	42				63	59	52	62
	0.95	38							
	0.95 - No MT-4	11	20			28			
S-2	1.00	44	65			67			74
	1.05	32							
	1.05 - No MT-4	23	35		35				

(a) Kilopoise. EOM = end of mix. Brookfield at 102°F. Total mix time = 170 minutes, including 90 minutes after solids addition complete and 30 minutes after curative addition. EOM viscosity measured 15 ±5 minutes after termination of mixing.

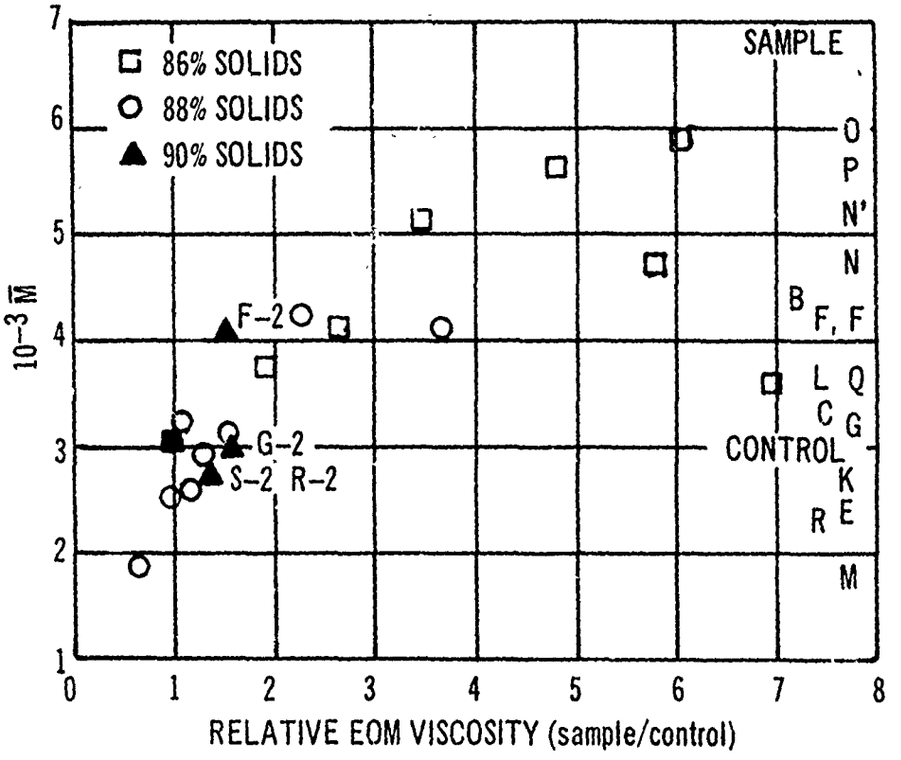

Figure 3 Relative End-of-Mix Viscosity versus $\overline{M}_n$

TABLE VI

RELATIVE PROPELLANT VISCOSITY AFTER 3 HOURS AT 40°C[a]

Sample	Relative Viscosity
Control	1.0
F-2	1.3
G-2	1.6
R-2	1.4
S-2	1.7

(a) MT-4 formulations

b. Propellant Tensile Behavior

Uniaxial tensile properties at -65, 70, and 140°F were measured at a strain rate of 0.54 in./in./min using the minithin tensile specimens previously described (Ref 1).

(1) Summary of Conventional Tensile Parameters

Table VII summarizes, for all formulations tested, the values of tensile parameters as conventionally reported. These include initial modulus E_o, stress and strain at maximum load $(\sigma/\epsilon)_m$, and stress and strain at rupture $(\sigma/\epsilon)_b$. Additionally, swell and gel measurements, which are indicative of binder crosslink density, are included for each of the formulations tested. The effect of MT-4 is to "harden" the propellant at higher temperatures and to increase strain at -65°F.

(2) Comparison at Constant 75°F σ_m

To permit comparison of tensile properties under similar conditions, NCO/OH ratios were selected that produced values for σ_m at 75°F between 140 and 160 psi. Resultant conventional tensile parameters are given in Table VIII. On this basis none of the prepolymer samples is clearly superior to the control lot.

(3) True Stress/Strain Curves and Parameters

Figures 4 through 12 present true stress/strain curves at a single NCO/OH ratio for formulations both with and without MT-4; the ratio chosen was that closest to the value employed above. The tensile parameters from these curves are presented in Table IX. As with the laboratory samples, no clear superiority above the control lot over the full temperature range can be observed.

c. Propellant Fracture Mechanics

Crack propagation measurements were conducted at -65 and 70°F in an attempt to distinguish more clearly among the pilot plant samples. Propellant strips measuring 3 by 1 by 0.1 inch were bonded to wooden tabs along the 3- by 0.1-inch edges and, after a 0.5-inch edge cut was made, were pulled at a rate of 0.2 in./min. Stress and strain at initiation of cut growth were measured, as well as the subsequent rate of growth from 0.5- to 0.7-inch cut length.

Data scatter was such that the only significant difference observed (see Table X) was a larger critical stress and strain, and hence fracture energy, for F-2 propellant at 70°F. How meaningful a superiority this may be--for motor thermal cycling, for example--is not clear, although

TABLE VII

PROPELLANT MECHANICAL PROPERTIES AT 90 PERCENT SOLIDS[a]
(From Instron Load/Time Trace)

Sample	NCO/OH	Shore A EOC[b]	-65°F			+75°F			+140°F			Percent Gel[c]	Percent Swell[d]
			E_o	$(\sigma/\epsilon)_m$	$(\sigma/\epsilon)_b$	E_o	$(\sigma/\epsilon)_m$	$(\sigma/\epsilon)_b$	E_o	$(\sigma/\epsilon)_m$	$(\sigma/\epsilon)_b$		
Control (Lot 008281)	0.75	74/57	9,700	580/15	580/20	470	85/29	70/37	385	70/28	70/29	56.5	18.8
	0.80	80/67	17,000	600/14	600/16	740	140/26	140/28	530	120/28	120/30	65.2	17.6
	0.80[e]	69/60	12,000	520/10	470/15	420	70/22	70/28	300	60/24	60/28	63.5	32.0
F-2	0.95	85/75	12,000	590/11	590/13	640	170/26	170/29	630	130/26	130/28	71.1	15.4
	1.0	86/70	10,000	600/12	600/13	880	210/28	200/29	720	160/28	160/31	82.5	13.8
	1.0[e]	70/42	12,700	564/10	540/12	340	60/24	56/33	180	40/27	39/32	53.5	21.1
G-2	0.85	83/73	14,000	600/10	600/11	760	150/28	140/30	590	120/30	120/31	68.4	15.2
	0.85[e]	74/51	11,000	550/9	540/13	270	60/28	60/33	160	50/34	50/38	43.2	31.2
	0.90	85/76	10,000	610/12	610/12	980	190/25	190/26	760	160/26	160/26	74.8	15.3
R-2	0.90	78/55	12,000	640/12	640/13	390	90/32	90/39	230	60/35	60/38	55.1	17.5
	0.95	80/65	10,000	630/10	620/11	550	150/25	140/27	500	110/29	110/30	68.5	15.7
	0.95[e]	80/53	15,000	600/9	590/11	370	70/23	60/36	190	50/31	50/38	40.7	28.4
S-2	1.00	83/66	11,000	640/11	630/12	520	130/27	126/32	370	90/30	90/32	60.9	15.5
	1.05	88/7[illegible]	15,000	660/9	650/10	830	160/25	152/29	515	110/27	110/28	63.2	12.1

(a) Minithins. Triplicate specimen. $(\sigma/\epsilon)_m$ at maximum load. $(\sigma/\epsilon)_b$ at failure.

(b) EOC = end of cure. Initial/15 seconds

(c) Percent Gel = percent of original prepolymer plus curative which is insoluble in toluene.

(d) Percent Swell = weight of toluene swollen gel x 100/weight of dry gel.

(e) No MT-4

TABLE VIII

COMPARATIVE TENSILE PROPERTIES[a]

Sample	NCO/OH	$E_o/\sigma_m/\epsilon_m$[b] -65°F	75°F	140°F
Control (Lot 008281)	0.80	17,000/600/14	740/140/26	530/120/28
F-2	0.925[c]	13,000/580/10	540/150/25	590/120/25
G-2	0.85	14,000/600/10	760/150/28	590/120/30
R-2	0.95	10,000/630/10	550/150/25	500/110/29
S-2	1.05	15,000/660/9	830/160/25	515/110/27

(a) Comparison at NCO/OH ratio which has σ_m at 75°F between 140-160 psi. MT-4 formulations

(b) σ_m and ϵ_m at maximum stress from Instron curves

(c) Extrapolated from 0.90 and 0.95 NCO/OH

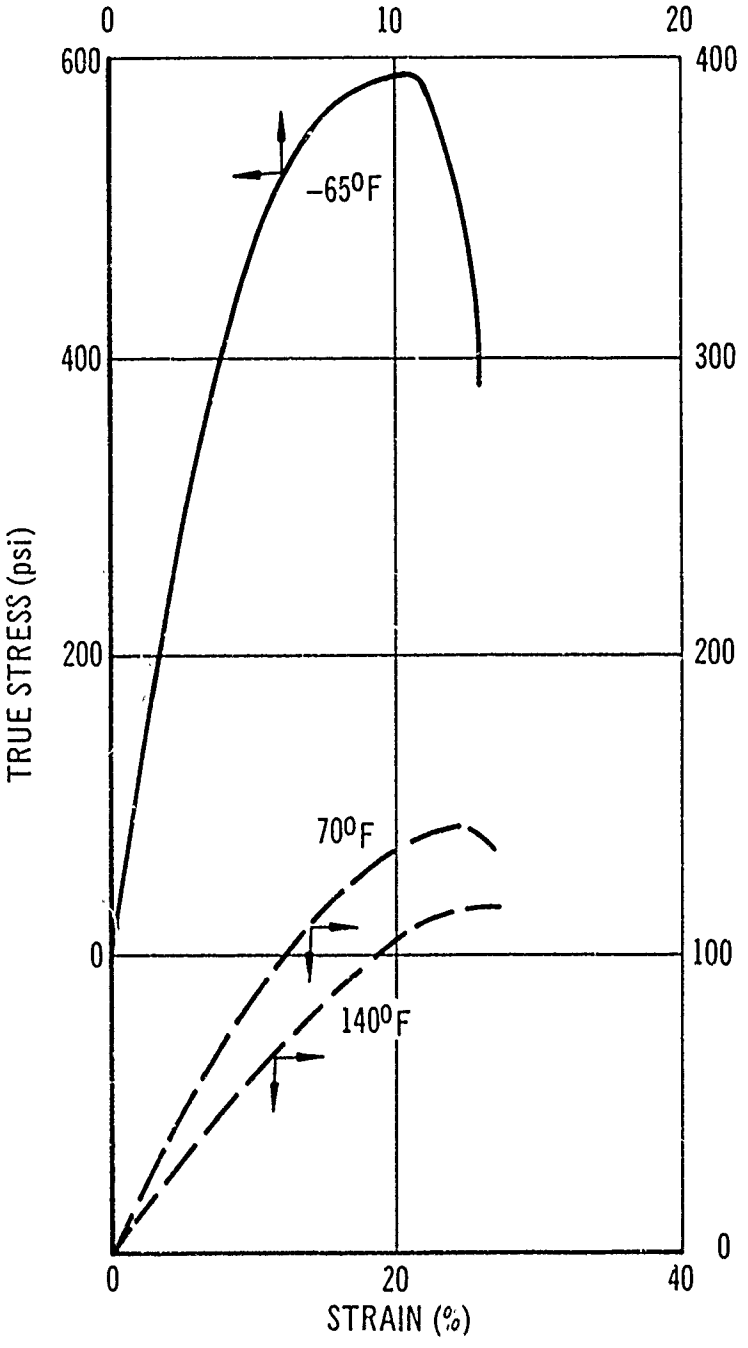

Figure 4 Tensile Behavior of Control Sample (90-percent Solids); NCO/OH = 0.80; 0.54 in./in./min

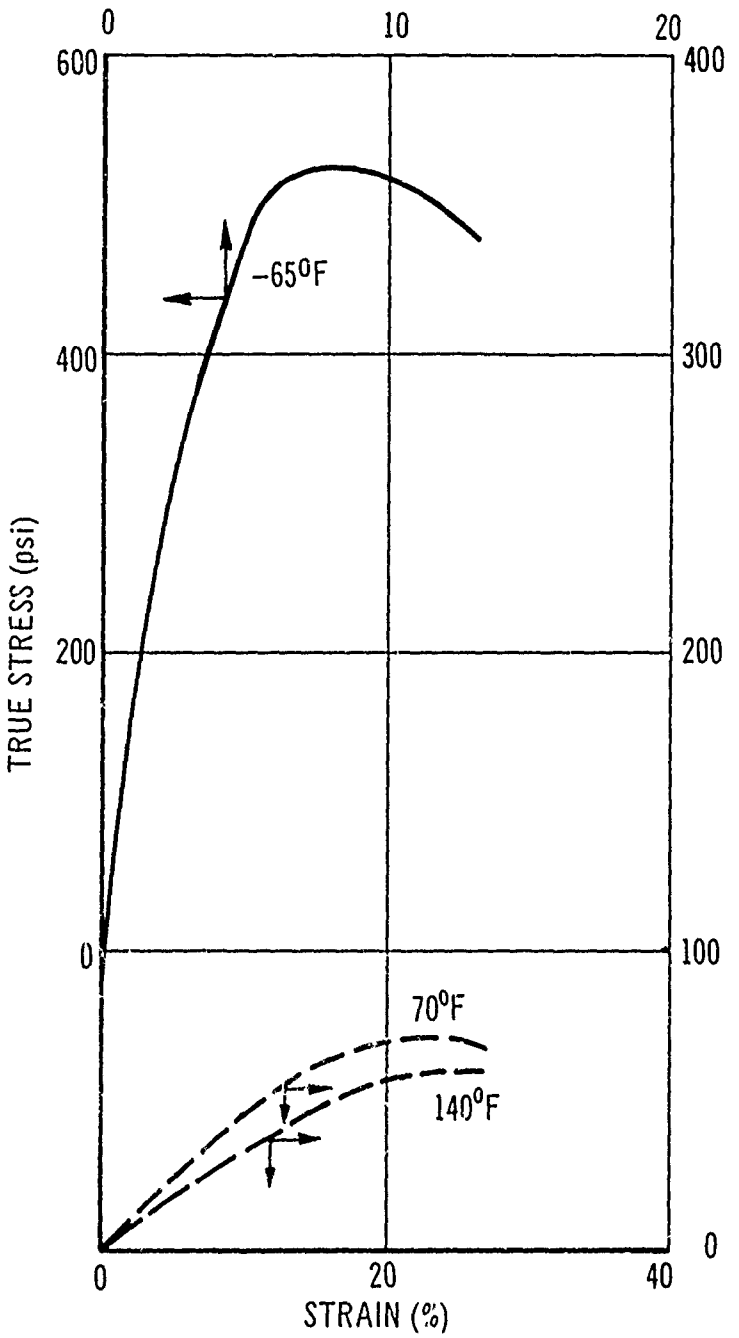

Figure 5 Tensile Behavior of Control Sample (90-percent Solids); NCO/OH = 0.80; No MT-4; 0.54 in./in./min

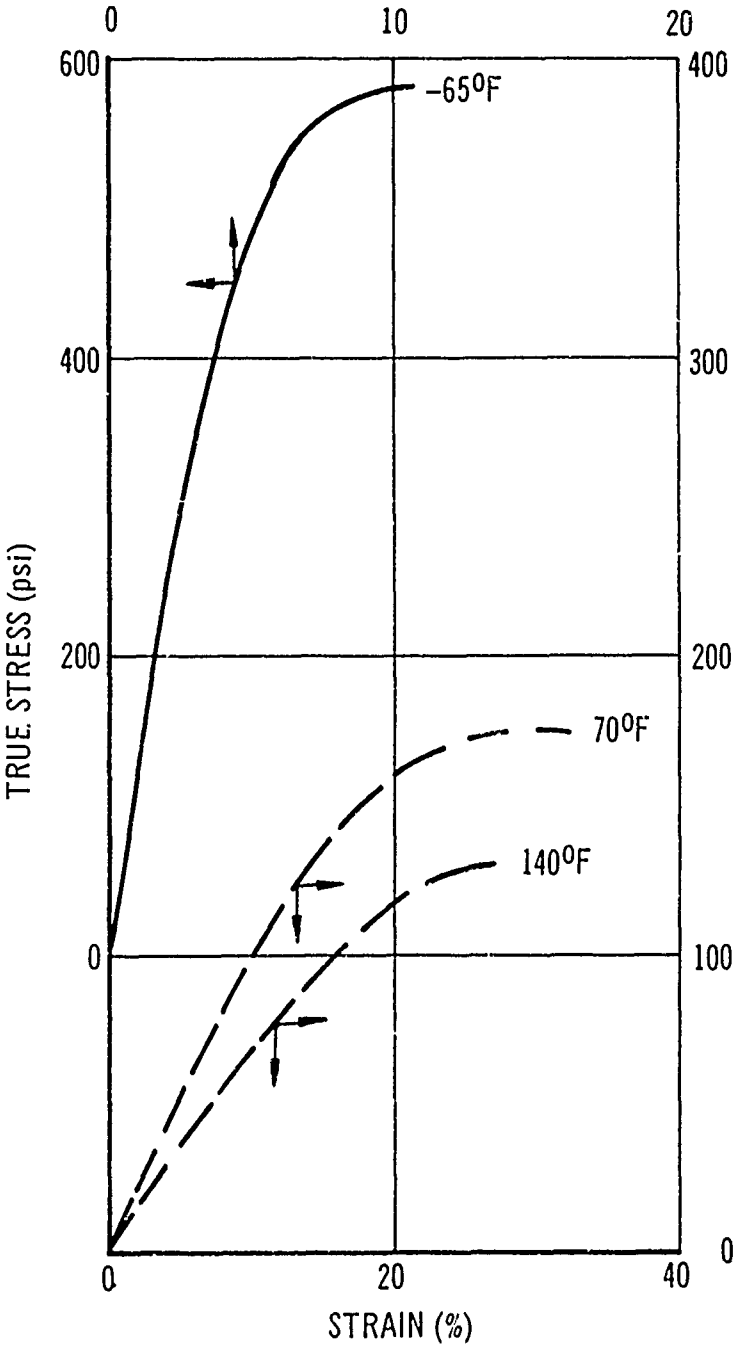

Figure 6 Tensile Behavior of Sample F-2 (90-percent Solids); NCO/OH = 0.95; 0.54 in./in./min

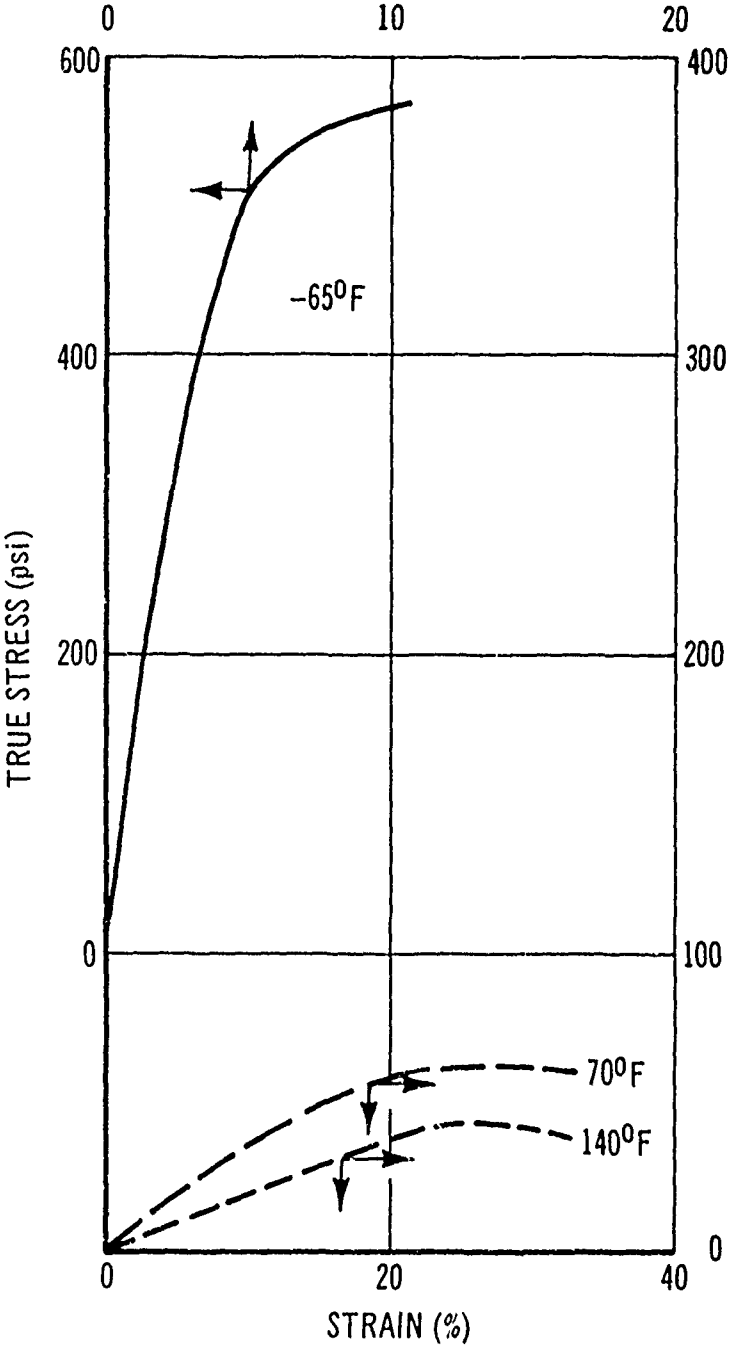

Figure 7 Tensile Behavior of Sample F-2 (90-percent Solids); NCO/OH = 1.0; No MT-4; 0.54 in./in./min

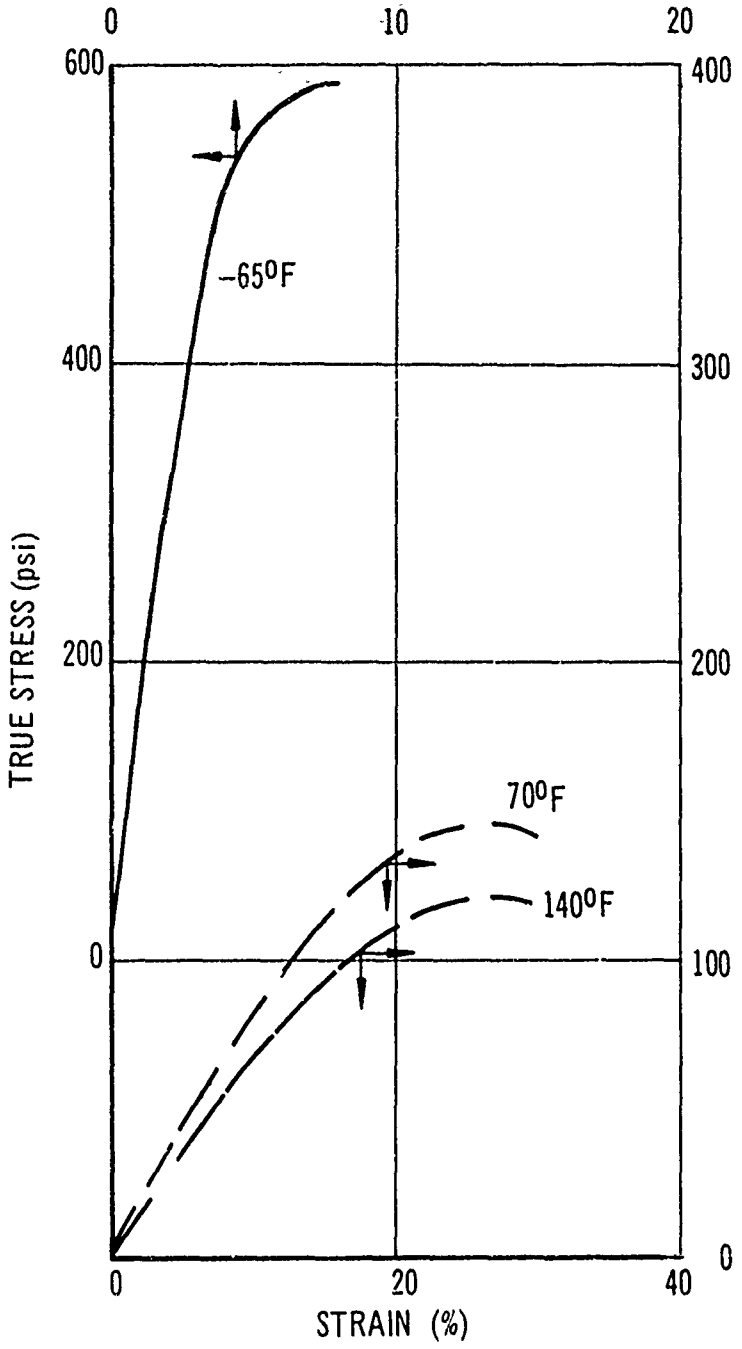

Figure 8 Tensile Behavior of Sample G-2 (90-percent Solids); NCO/OH = 0.85; 0.54 in./in./min

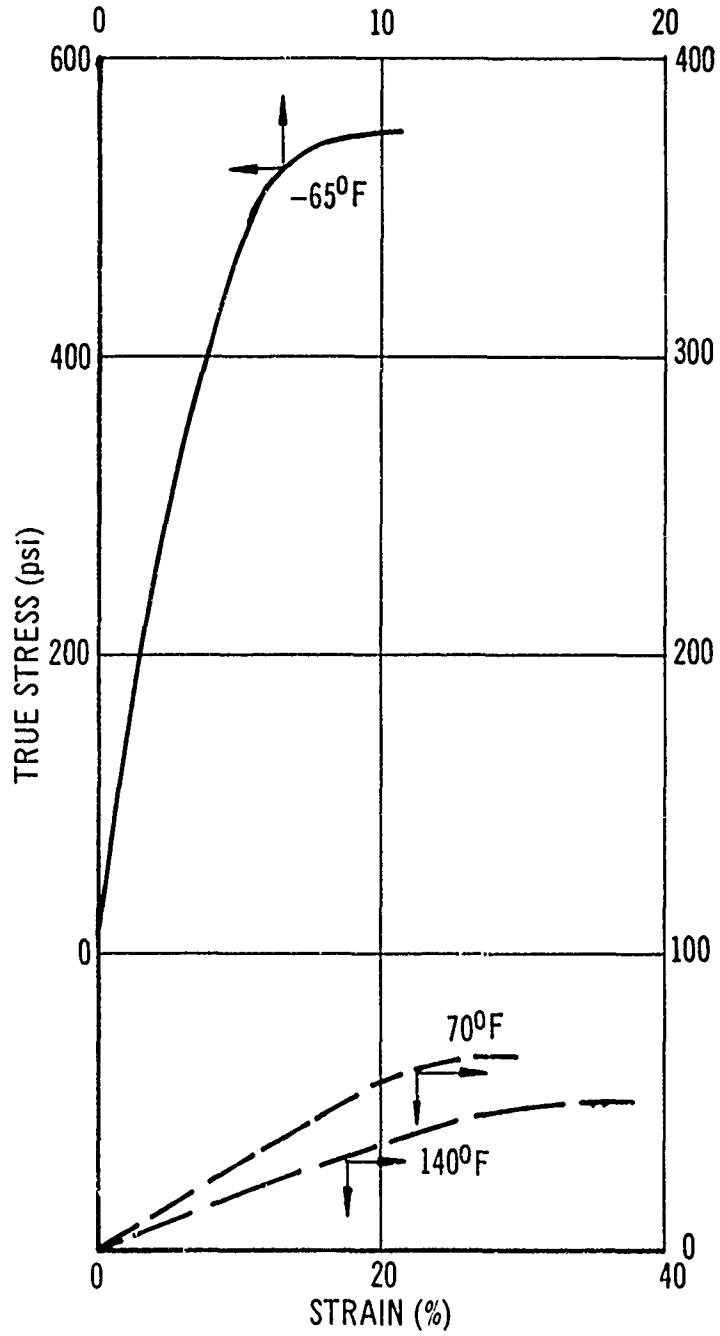

Figure 9 Tensile Behavior of Sample G-2 (90-percent Solids); NCO/OH = 0.85; No MT-4; 0.54 in./in./min

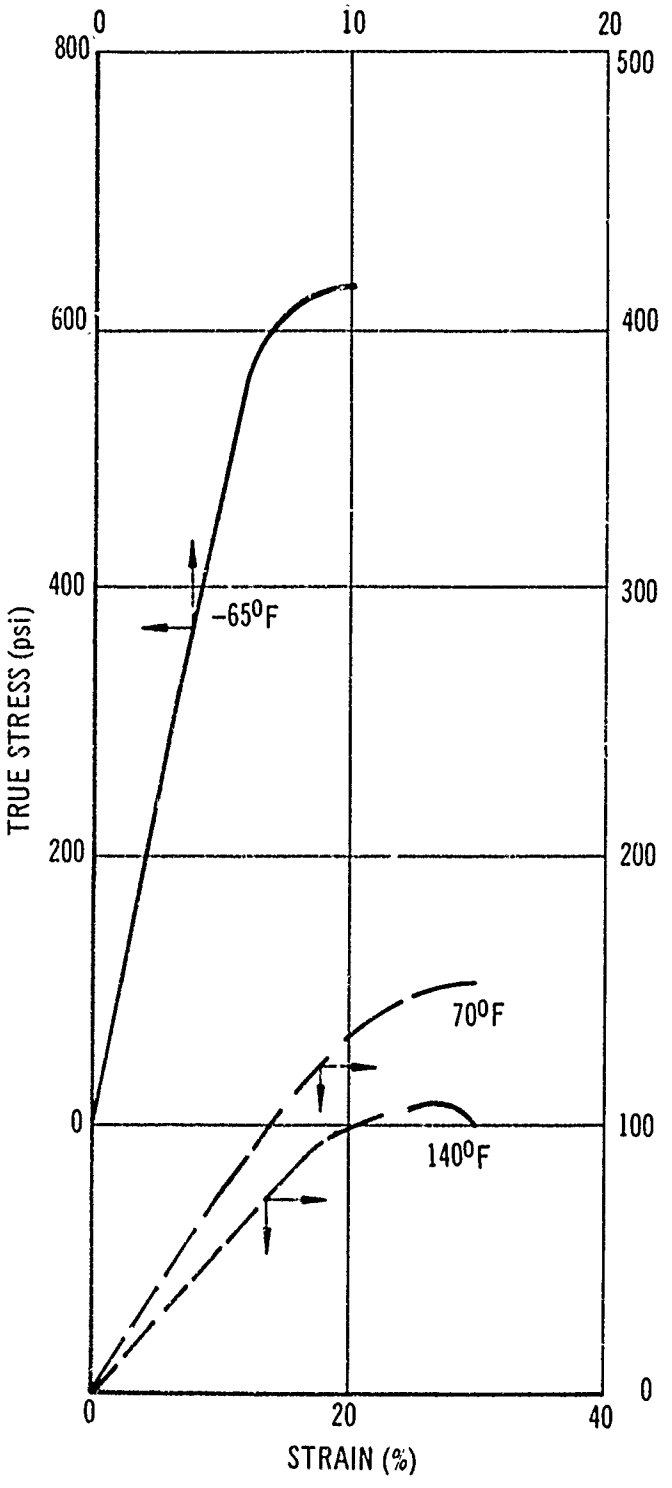

Figure 10 Tensile Behavior of Sample R-2 (90-percent Solids); NCO/OH = 0.95; 0.54 in./in./min

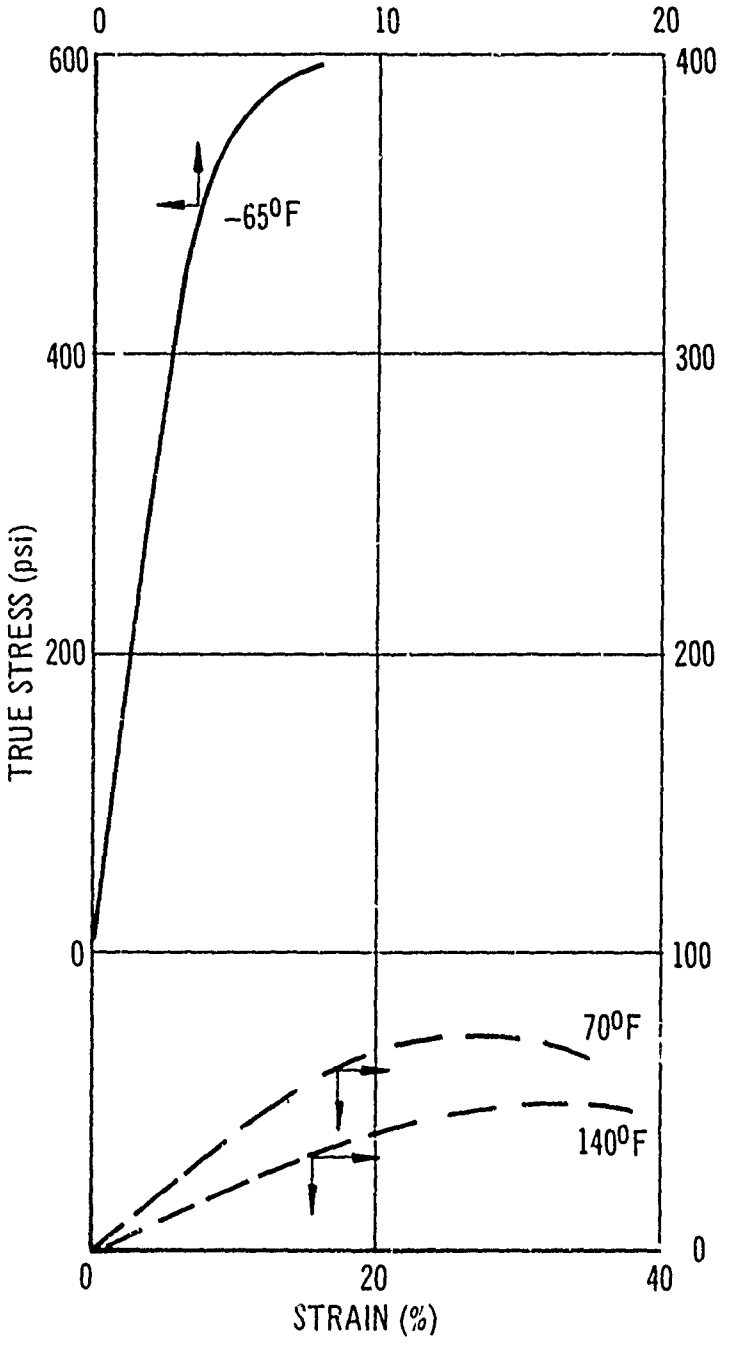

Figure 11 Tensile Behavior of Sample R-2 (90-percent Solids); NCO/OH = 0.95; No MT-4; 0.54 in./in./min

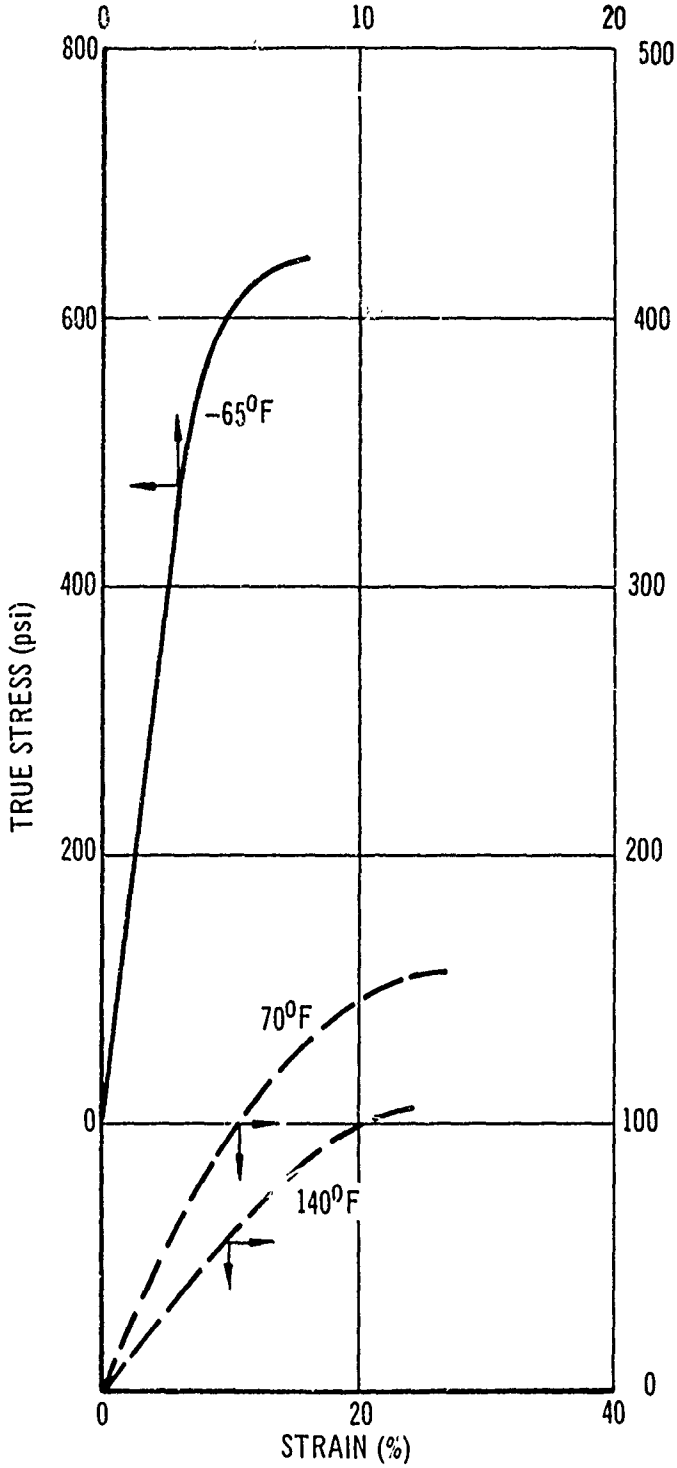

Figure 12 Tensile Behavior of Sample S-2 (90-percent Solids); NCO/OH = 1.05; 0.54 in./in./min

TABLE IX

TENSILE PARAMETERS FROM TRUE STRESS/STRAIN CURVES FOR 90 PERCENT SOLIDS PROPELLANT

Sample	NCO/OH	-65°F				+75°F				-140°F			
		E_o	Yield[a]	Maximum[a]	Rupture[a]	E_o	Yield[a]	Maximum[a]	Rupture[a]	E_o	Yield[a]	Maximum[a]	Rupture[a]
Control (Lot 008281)	0.75	9,700	325/2	560/16	560/19	470	65/12	80/27	80/29	390	50/12	65/21	65/27
	0.80[b]	12,000	320/2	575/8	475/13	420	50/11	70/23	70/23	300	50/18	60/24	60/27
	0.80	17,000	410/3	590/11	380/14	740	100/11	140/24	40/27	530	85/12	120/25	110/27
F-2	0.95	12,000	450/4	580/11	---	640	130/12	170/27	170/33	630	100/15	130/27	---
	1.00	10,000	475/5	590/11	---	880	180/17	210/27	200/30	720	120/15	160/27	160/30
	1.00[b]	12,700	450/4	570/11	---	340	45/12	60/27	55/32	180	40/21	45/27	35/32
G-2	0.85[b]	11,000	410/3	550/11	---	270	60/21	65/30	---	160	45/25	50/38	---
	0.85	14,000	500/4	590/8	---	760	110/13	150/27	140/30	590	95/15	120/27	120/30
	0.90	9,800	540/5	600/11	---	980	160/14	190/24	---	760	140/17	160/25	---
R-2	0.90	12,000	500/4	640/11	---	390	70/16	90/30	90/35	230	50/18	60/32	60/35
	0.95	9,800	560/6	630/11	---	550	120/16	150/30	---	500	95/18	110/27	100/30
	0.95[b]	15,000	500/4	590/8	---	370	60/15	70/33	65/35	190	35/18	50/32	50/38
S-2	1.00	11,000	530/5	620/8	---	520	100/16	130/32	---	370	65/15	90/30	---
	1.05	15,000	550/3	640/8	---	830	100/10	160/27	---	520	80/14	110/24	---

(a) Values of σ/ϵ

(b) No MT-4

TABLE X

PROPELLANT CRACK PROPAGATION [a]

Sample	NCO/OH	-65°F				+70°F			
		σ_c [b]	ϵ_c [c]	Γ_c [d]	Rate [e]	σ_c [b]	ϵ_c [c]	Γ [d]	Rate [e]
Control	0.90	290	5.4	2.8	0.05	75	6.0	0.8	0.6
F-2	0.95	380	4.0	2.7	0.1	110	9.0	1.8	0.6
G-2	0.85	430	4.6	3.5	0.1	68	7.4	0.9	0.5
R-2	0.95	325	4.0	2.3	0.1	64	7.3	0.8	0.5

(a) Constant elongation rate (0.2 in./min). Specimen 1 x 3 x 0.1 in. Initial edge cut of 0.5 in. Triplicate specimens at 70°F and at least duplicate at -65°F.

(b) Critical stress, psi.

(c) Critical strain, %.

(d) Fracture energy, lb/in.

(e) Rate of crack growth from 0.5 to 0.7 in.

it seems possible that F-2 at a lower NCO/OH ratio might possess improved crack resistance while maintaining high-temperature capability.

d. Strain/Temperature Cycling of JANNAF Specimens

Since neither the tensile nor the crack propagation data gave evidence of major differences among the propellants, the feasibility of a laboratory test for evaluating relative capability to withstand motor thermal cycling was examined. Standard JANNAF specimens (four of each propellant in parallel) were slowly strained on an Instron tester from 0 to 15.5 percent, while the temperature was simultaneously decreased from 140 to -65^{0}F over a 90-minute period. The cycle was then reversed to permit return within 90 minutes to the original crosshead displacement and to 140^{0}F. Total load for the four specimens was recorded continuously.

Available data are summarized in Table XI in terms of the rate of load reduction (-65^{0}F) and qualitative observations of sample damage. Although these results must be considered highly preliminary, they indicate definite potential for laboratory characterization of thermal cycling capability and the possibility of improved behavior for R-2 and S-2.

3. CONCLUSIONS

(1) Good duplication is shown between ARCO's laboratory and pilot plant processing.

(2) Propellant processability with the pilot plant samples is poorer than with standard R-45M. This may be partially a reflection of higher contents of residual catalytic impurity (iron compounds) resulting from limited use of the pilot plant reactor.

(3) On the basis of the tests employed in evaluating mechanical behavior, no clear superiority is apparent for pilot plant samples relative to standard R-45M.

TABLE XI

TEMPERATURE/STRAIN CYCLING RESULTS

Sample	NCO/OH	Load Reduction Rate[a]	Number Cycles and Specimen Condition[b]
Control	0.80	9	23 full cycles; 3 specimens broken and 1 with no cracks
F-2	0.95	7	36 full cycles plus 7 cycles without cooling (between 13th and 14th full cycles); 3 specimens with cracks and 1 uncracked
R-2	0.95	4	38 full cycles; 3 specimens cracked, 1 failed after 30 cycles
S-2	1.05	2	35 cycles; 1 specimen failed, 3 with cracks

(a) Pounds per cycle. Slope of straight line through maximum load (-65 degrees)/cycle plot.

(b) Three-hour cycle. Visual observation of condition.

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SECTION IV

FUTURE WORK

The original program plan called for final evaluation of one pilot plant prepolymer at the 10-gallon mix level with emphasis upon analog motor thermal cycling tests. In view of the results obtained to date and with the realization that different temperature cycling behavior may not be apparent from uniaxial tensile data, the program has been redirected to permit a more detailed evaluation of three pilot plant samples (F-2, R-2, S-2) at the 1- or 2½-gallon mix level. For each of these prepolymers and control, thermal cycling capability will be compared using analog motors as well as the laboratory strain/temperature cycling test.

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Appendix A

LABORATORY SAMPLE CHARACTERIZATION SUMMARY

Parameter	Sample															
	RR[1]	B	C	E	F	G	K	L	M	N	N'	O	P	Q	R	Control[2]
$\bar{M}_n$ (VPO)																
Mean	2700	4200	3150	2590	4100	3100	2890	3600	1850	(4720)	(5100)	5840	5560	3750	2530	3000
RSD[3]	1.7%	7.3%	3.8%	3.0%	5.7%	7.4%	7.2%	4.5%	2.4%			4.5%	15.8%	12.3%		
$\bar{M}_n$ (GPC)	2930	3840	3050	2520	3830	2960	2800	3620	2260	5510	4330	5680	4800	3930		
$\bar{M}_w/\bar{M}_n$ (GPC)	1.66	1.94	1.72	1.63	1.68	1.56	1.52	1.93	2.29	2.20	1.79	1.88	1.83	1.53		
$\bar{M}_w$ (GPC)	4900	7450	5250	4100	6450	4600	4250	7000	5200	10400	7750	10200	9050	7200	3420	
Eq. Wt. (TSI)																
Mean	1220	2180	1630	1360	2270	1770	1500	1930	900	3300	3030	3180	3070	2180	1220	1290
RSD[3]	2.1%	3.3%	4.2%	3.0%	3.5%	2.6%	2.8%	3.5%	3.3%	4.7%	2.1%	2.6%	6.2%	2.2%		
Eq. Wt. (AA)																
Mean	1320	2380	2690	1470	2380	1730	1640	2080	1050	3330	3230	3330	2170	1280		
$\bar{f}_n$[4]																
Mean	2.21	1.93	1.93	1.91	1.81	1.75	1.93	1.87	2.05	(1.43)	(1.68)	1.84	1.8'	1.72	2.08	
RSD[3]	3.8%	10.6%	8.0%	6.0%	9.2%	10.0%	10.0%	8.0%	5.7%			7.1%	22.0%	14.5%		
$\bar{f}_w$[5]																
Mean	2.36	2.45	2.15	2.33	2.03	2.04	2.14	2.36	2.67	2.07	2.31	2.08	2.18	2.27	2.10	2.42
RSD[3]	1.9%	2.2%	1.0%	7.3%	0.4%	1.4%	3.1%	6.3%	1.3%	1.5%	1.6%	1.9%	6.4%	5.1%		
η[6]	43	182	60	35	112	54	40	100	42	400	340	500	400	200	35	49
Reactivity[7]		0.29	0.28	0.33	0.42	0.18	0.29	0.85	0.55	0.13	0.26	0.15	0.17	0.18	0.32	0.37

(1) Round Robin R-45M Lot 110225
(2) R-45M Lot 008281
(3) Relative Standard Deviation for all data points
(4) $\bar{M}_n$/TSI equivalent weight
(5) From degree of DDI conversion at incipient gelation (ambient temperature.
(6) Brookfield at 30°C. Poise
(7) Relative reactivity. Fraction of NCO (DDI) reacted after 10 hours at ambient. From reaction profile for determination of f_w.

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